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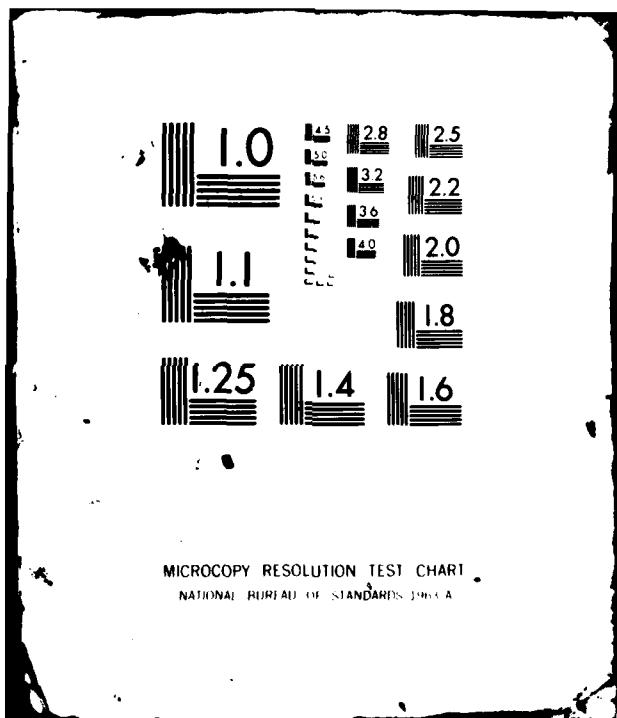
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THE COMBUSTION OF ALTERNATE
FUEL SYSTEMS

SHOCK TUBE STUDIES OF THE DECOMPOSITION
OF ORGANIC MOLECULES

FINAL REPORT

FEBRUARY, 1982

PREPARED FOR
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SUMMARY

This report summarizes a series of shock tube experiments, which were carried out at the Naval Research Laboratory under Contract No. N00014-80-C-0462 during the time period May 18, 1980 to August 18, 1981. During this time period, a CO laser was calibrated for the purpose of monitoring CO formation rates during the decomposition of several organic molecules. The compounds investigated were formic acid (HCOOH), formaldehyde (HCHO), ketene (CH_2CO), and cyclobutanone ($\text{C}_4\text{H}_6\text{O}$). The decomposition data are under analysis at NRL.

The experiments were carried out in the shock tube facilities as part of an NRL Chemistry Division program. The Geo-Centers effort assisted in the data collection and analysis for the CO laser calibration and subsequent absorption measurements for the indicated organic molecules. The NRL personnel involved in the program include Dr. M. C. Lin, Dr. D. Hsu, Dr. W. Shaub and Mr. T. Creamer.

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INTRODUCTION

The performance and availability of fuels for internal combustion engines is of vital strategic importance to the U.S. Navy. One method of reducing our dependence on foreign oil imports is the use of alternate fuels derived from shale oil or liquified coal. A thorough knowledge of the combustion chemistry of organic molecules is, therefore, necessary in order to be able to assess the suitability of such fuels.

It is already known that intermediate species such as formaldehyde, formic acid, ketene, and cyclobutanone, play an important role in the decomposition of many hydrocarbon fuels. Chemical kinetic considerations suggest that decomposition of these molecules results in CO-formation, and therefore, monitoring of CO production rates is one way of obtaining valuable information about the kinetic processes which are occurring.

A very convenient way of measuring time resolved CO concentration profiles is through the absorption of CO laser energy. Furthermore, if the absorption experiments are carried out behind reflected shock waves in a shock tube, very careful control over temperature, pressure, and initial reactant concentrations can be achieved, resulting in a high degree of accuracy in measured kinetic rate constants.

This report summarizes several shock tube experiments which were conducted in order to develop the apparatus and technique for CO absorption measurements. The major emphasis is on stabilization and calibration of the CO laser used. Once the calibration was completed, CO formation was studied with several test gases including ketene (CH_2CO), formic acid (HCO_2H), formaldehyde (HCHO), and cyclobutanone ($\text{C}_4\text{H}_6\text{O}$). Much of the data collected is still being analyzed, and will be published later in appropriate journals.

EXPERIMENTAL ARRANGEMENT

A. Description of the Shock Tube System

A schematic of the shock tube - laser probing apparatus is shown in Fig. 1. The entire tube and vacuum line were made of type 316 stainless steel and were pumped by a 6-inch diffusion pump. The tube has a 6.35 cm inside diameter and a highly polished inside surface (r.m.s. finish of $6\mu\text{m}$). The driver and test sections are $2.52\mu\text{m}$ and $3.80\mu\text{m}$ long, respectively, in the reflected shock configuration, and are mounted on a center block in which a diaphragm could be held by compression between two "O" rings.

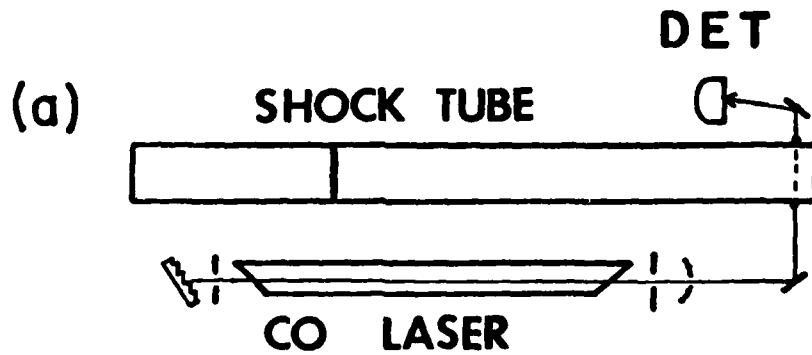


Figure 1. Schematic of the shock tube - CO laser probing apparatus.

The velocity of the shock front was monitored by four BaTiO₃ piezoelectric pin gauges. The first gauge, used for triggering electronics, was located 309.0 cm from the diaphragm station. Successive gauge spacings were 35.06 cm, 19.94 cm, and 20.02 cm downstream. Shock pressure traces were monitored with a quartz transducer located 4.5 cm from the end plate (in the reflected shock configuration). Two pairs of optical ports with MgF₂ windows were perpendicular to the shock tube and also located 4.5 cm from the end plate. The optical ports were internally rounded to the same internal diameter as the shock tube. The MgF₂ windows were 0.95 cm diameter and 0.64 cm thick. In the incident shock experiments a 61 cm extension of the test section was used.

B. CO Laser Calibration

A stabilized CW CO laser was used to probe the CO formed in various decomposition reactions. A liquid nitrogen cooled laser tube with about 1.2 cm diameter and an active length of about 1 m was sealed by a pair of BaF₂ Brewster windows. The laser gases, He (4 Torr), N₂ (2 Torr), CO (~0.1 Torr) and NO (trace) were admitted through a sidestream near the electrode at one end of the laser tube and pumped out continuously through another sidearm near the electrode at the other end of the tube. The laser cavity was formed by a 3 m radius output coupling mirror (with about 3% transmission between 4.7 and 6.0 μ m) and a 240 lines/mm grating (blazed at 3.75 μ m), as shown in Figure 1. Two variable irises were placed in the laser cavity, one in front of the output coupling mirror and the other in front of the grating to enable single mode (TEM₀₀) operation

for the various laser lines. The output coupling mirror was mounted on a piezoelectric transducer which continuously stabilized the laser to line center.¹

The output of the CO laser was directed perpendicularly to the shock tube through a pair of optical ports fitted with the MgF₂ windows. The CO radiation transmitted through the shock tube impinged on a lead block diffuser (i.e., a flat lead brick surface treated with fine sand paper), and the diffuse radiation was detected by an InSb detector maintained at 77 K. The detector signal was amplified by a Tektronix 7A13 differential amplifier and was displayed on a Tektronix 7633 storage oscilloscope.

In all of the absorption measurements, the 2+1 P(10) transition of the CO laser was used rather than the 1+0 transition because of its much greater laser stability. In a typical absorption measurement, the shock tube was first diffusion-pumped for at least 15 min. to $\leq 10^{-4}$ Torr before the mixture was admitted into the driven section. Then the driver section was pressurized with helium until the mylar diaphragm burst. All calculations for shocked gas properties such as temperature, pressure and density were made by using the NASA/LEWIS² equilibrium program. Frozen flow conditions were assumed to exist immediately behind the shock wave.

Research grade CO (99.99% purity) used in the calibration measurements and ultra-high purity grade Ar (99.999%) were obtained from the Matheson Gas Products Company. Before use, CO was purified by passing it through two liquid N₂ cooled traps to remove any condensable materials. Calibration gases containing 0.357%, 0.711% and 1.420% CO in argon were mixed manometrically, and allowed to stand for several days before use.

Calibration experiments were carried out behind reflected shock waves at temperatures ranging from 1550 to 3260 K and pressures from 1.6 to 4.8 atmospheres. The absorption measurements were taken with the CO laser operating on the 2+1 P(10) transition probing the v = 1 population, which in turn is related to the total CO concentration through the Boltmann distribution.

The amount of CO laser energy absorbed by the shocked gas is a function of the number of absorbers (CO molecules) present in the gas volume irradiated by the laser, and also the strength of absorption per molecule. The absorption linewidth for a given vibrational transition is strongly temperature and pressure dependent over the range of experimental conditions investigated here. For this reason, temperature-induced shifts in vibrational energy level populations, as well as Doppler and pressure broadening had to be accounted for in the calibration.

The absorption for P-branch transitions is given by 3-6,

$$\alpha(v, J) = \frac{8 (\ln 2)^{1/2} \pi^{5/2}}{3kT} \frac{v}{\Delta v_D} \left| R_V \right|^2$$

$$\times F_{vr} J N_v \exp(-\chi^2) \operatorname{erfc}(\chi) \quad (1)$$

$$\times \left\{ \left(\frac{N_{v+1}}{N_v} \right) B_{v+1} \exp \left[-B_{v+1} J (J-1) hc/kT \right] \right.$$

$$\left. - B_v \exp \left[-B_v J (J+1) hc/kT \right] \right\}$$

where

$$\chi = (\ln 2)^{1/2} \Delta v_L / \Delta v_D \quad (1a)$$

$$\Delta v_L = \gamma^\circ P (300/T)^{0.73} \quad (1b)$$

$$\Delta v_D = v (2kT \ln 2/mc^2)^{1/2} \quad (1c)$$

Here, v and J represent the vibrational and rotational quantum numbers of the lower absorption level. B_v is the rotational constant for the v th vibrational level, $\left| R_V \right|^2$ is the rotationless matrix element for the $v \rightarrow v+1$ transition, F_{vr} is the Herman-Wallis factor, Δv_D is the Doppler half-width, Δv_L is the Lorentz half-width, P is pressure in atm. and N_v is the population of the v th level. The value of the exponent for the temperature term, 0.73, in Eq. (1b) was used instead of the commonly employed value of 1/2, in accordance with the recent finding of Hanson.⁷

The rotational constant for each level was computed from¹

$$B_v = B_e - \alpha_e (v+1/2) + \chi_e (v+1/2)^2 \quad (2)$$

The values of the molecular constants used in equations (1) and (2) are given in Table 1.

Table 1 - Molecular Constants Used for
Calculation of CO Absorption
Coefficients

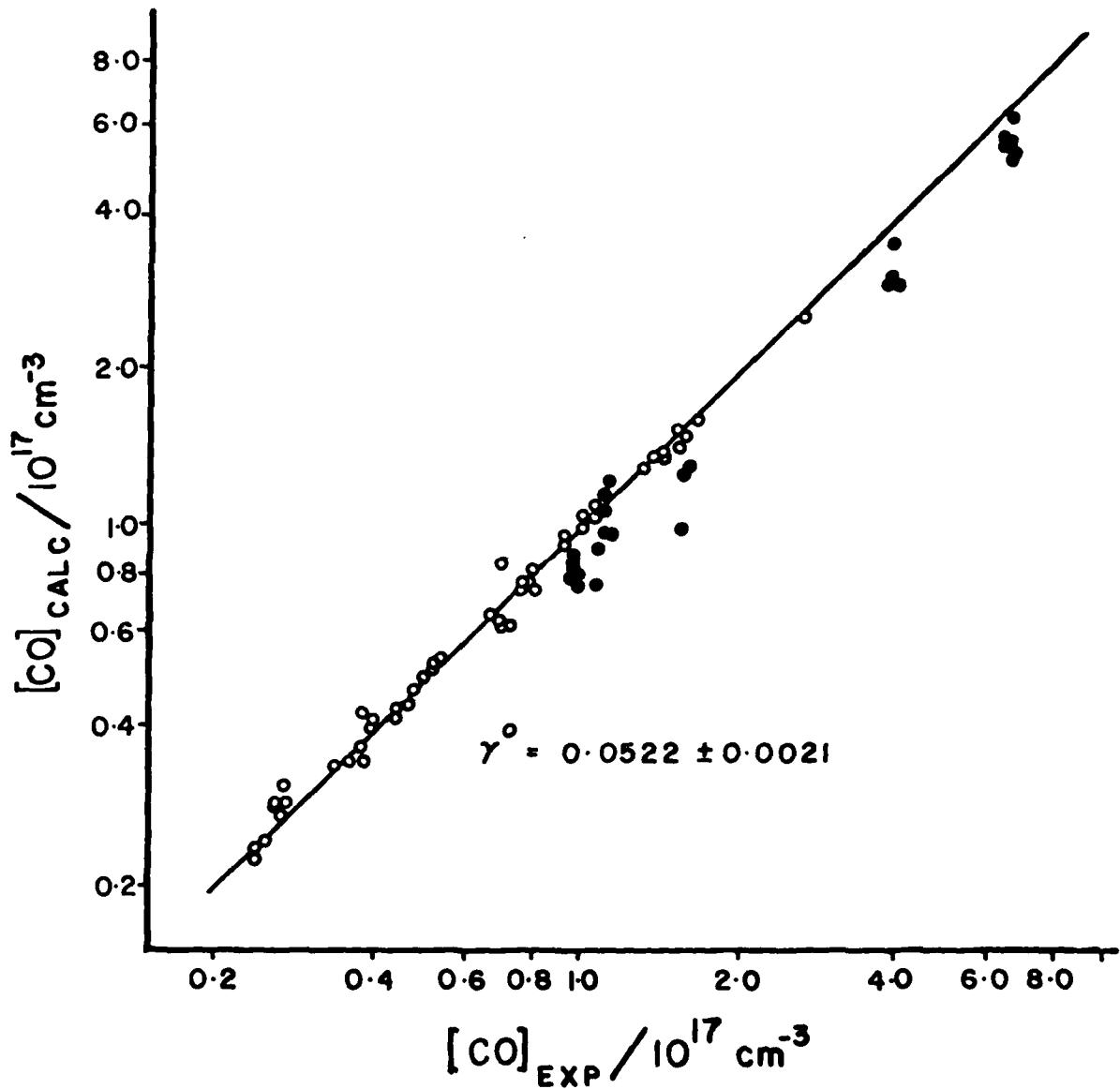
B_e	1.931271 cm^{-1}	reference 1
α_e	0.017513 cm^{-1}	reference 1
γ_e	$2.96 \times 10^{-6} \text{ cm}^{-1}$	reference 1
R_o	0.104 debye	reference 1
$ R_1 ^2/ R_o ^2$	2.0	reference 8
$ R_2 ^2/ R_o ^2$	2.99	reference 8
F_{vr}	1.00355	reference 1

For each calibration run, the equilibrium temperature and CO concentration in the sample volume were computed with the NASA Lewis code based on the known initial concentration and the measured shock velocity. The absorption coefficient for each run is given by,

$$x = \ln (I/I_0)/D \quad (3)$$

where I_0 and I are the CO laser intensities before and after the arrival of the reflected shock, and D is the diameter of the shock tube, 6.35 cm.

The calibration requires that the CO concentration calculated from Eq. (1) using the absorption data be equal to the known CO concentration in the shocked mixture. This could be accomplished by determining the appropriate, only unknown parameter γ^0 , the room temperature Lorentz half-width in Eq. (1b) which reflects the extent of pressure-broadening. Figure 2 presents calibration data obtained with and without lock-in stabilization of the laser, shown by the open and filled circles, respectively. With a value of $\gamma^0 = 0.0522 \pm 0.0021 \text{ cm}^{-1} \text{ atm}^{-1}$, an excellent calibration for CO could be obtained (i.e., the open points could be correlated with a line of unit slope). The difference between the open and filled data points shows the importance of the lock-in stabilization of the CO laser. The value of γ^0 obtained agrees very well with that reported by Hanson,⁷ $0.0475 \text{ cm}^{-1} \text{ atm}^{-1}$.



EXPERIMENTAL RESULTS

A. HCOOH Decomposition Data

Incident and reflected shock experiments have been carried out in a temperature range from 1280 to 2030 K for HCOOH/Ar mixtures varying from 0.07% to 1.64%. The mixtures were prepared from formic acid (99% purity) obtained from K and K Laboratories, Inc. Additional purification was accomplished by refluxing it with B_2O_3 (which was prepared from boric acid by prolonged heating above 169°C) under dry air and distilled over at 101°C.⁹

In the preparation of HCOOH/Ar mixtures, the concentration of dimers, $(CHOOH)_2$, was taken into consideration. The equilibrium constant K , in atmosphere units, for the reaction:



was taken as ¹⁰

$$\log K = 5.62919 - 2985.33/T + 0.76044 \log T \quad (4)$$

At the low temperature at which the test mixtures were prepared, a considerable number of dimers will be present in the mixture. For instance, a 2 Torr sample at 22°C should contain about 40% dimers. Equation (4) predicts only a negligible amount of dimers to exist at the elevated temperatures behind reflected shocks. Therefore, the HCOOH mole fraction quoted for each mixture refers to that at high temperature only, and is the same as that of total carbon.

In all the runs, the $2 + 1 P(10)$ transition of the CO laser was used for the absorption measurements. Figure 3 shows a typical oscillosograph for a single shock experiment. The upper trace is the CO absorption trace, and the lower trace is the pressure trace as registered by the quartz pressure transducer at the observation station. By use of the calibrated absorption Eq. (1), and the Boltzmann equation for CO vibration-rotation population distribution, the absorption data can be readily converted into CO concentration-time profiles.

(b)

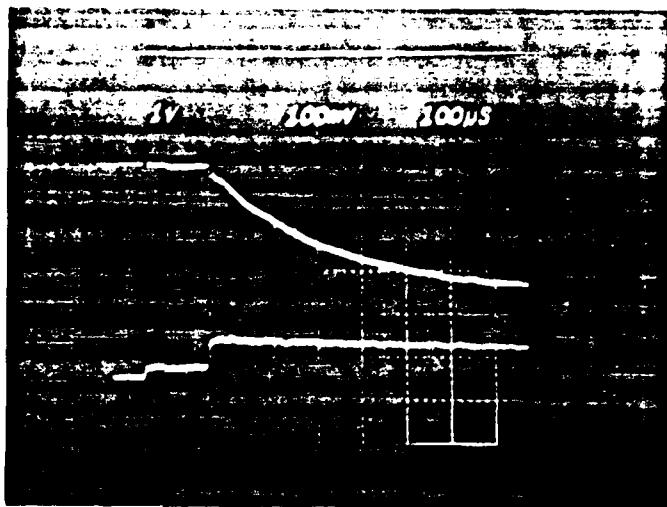


Figure 3. Typical oscillograph. Upper trace is an absorption curve measured on the InSb detector and lower trace is a pressure profile monitored by the quartz pressure transducer. In the shocked gas: $T = 1478$ K, $P = 2.168$ atms and mole fraction of $\text{HCOOH} = 0.775\%$.

Several shock tube runs have been made over the temperature range indicated above, and the data are being reduced in order to obtain rates of CO formation as a function of time after passage of the reflected shock. The rate data will be analyzed to determine the most probable kinetic mechanisms for HCOOH decomposition. Both molecular and radical mechanisms will be considered. The data analysis is being continued in the Chemistry Division at NRL, and the results will be published at a later date.

B. Ketene

Additional absorption experiments were performed behind reflected shock waves in mixtures containing small quantities of ketene in argon. Initial results produced ambiguous profiles of CO absorption vs. time. After examination of sample purity and stability, a new sample preparation was attempted. Repetition of the experiments yielded similar results. These results were later interpreted in the light of the cyclobutanone data, given below.

C. Cyclobutanone:

Initial shocks of cyclobutanone in Ar yielded reasonable absorption vs. time traces. However, reduction of the raw data to an absolute number density of CO as a function of time resulted in CO production which exceeded the original carbon present in cyclobutanone by approximately a factor of 10. Two possibilities were considered:

(1) the absorption coefficient for CO was in error and too large by this amount; or

(2) the assumed cyclobutanone concentrations were incorrect due to improper preparation or dilution.

New samples were prepared and new dilutions made, but the results did not change. It was decided that the apparent magnitude of the absorption coefficient would appear large if a species besides CO were present which also absorbed CO laser radiation. An examination of the absorption spectrum of each of the expected products of cyclobutanone decomposition revealed that ketene was a likely candidate in this role. If ketene does absorb the CO laser line used, then the total attenuation of the laser beam is a function of the concentration of both CO and ketene. This explanation is also helpful in accounting for the ketene results mentioned above: as a function of time, a shocked ketene mixture contains a decreasing concentration of absorbing reactant and an increasing concentration of absorbing product, CO, yielding a total attenuation that cannot be simply related to the concentration of either species alone. This difficulty can be overcome by choosing a laser frequency which is absorbed by CO only. The proposed absorption by ketene of the laser radiation introduces the possibility of determining not only CO number densities but also ketene number densities. Recalibration of the experimental system with ketene in place of carbon monoxide is necessary to achieve this measurement. Serious consideration of this approach will be deferred until after a thorough analysis of the data, which is in progress.

D. Formaldehyde

A few preliminary runs were made with test mixtures of formaldehyde in Ar. It was decided that analysis of the data and subsequent experiments should not be attempted until after the formic acid has been satisfactorily interpreted. This effort will be performed by NRL.

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